ROTATIONAL STRUCTURE OF λ 3600 – λ 3200 A. BANDS OF Na_2 *

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ABSTRACT. The λ3132Å (2, 3), λ3150Å (2, 4) and λ3168Å (2, 5) bands of the λ3600–λ3200 A system of Na_2 have been photographed in the first order of a 21-ft. concave grating with a dispersion of about 1·3 Å per mm and an attempt has been made to study their rotational structure. Each band is found to consist of a single P and a single R branch, characteristic of a $^1\Sigma - ^1\Sigma$ transition. The lower state is known to be a $^1\Sigma_g^+$ state due to $3\,^2S + 3\,^2S$ atoms of sodium. Hence the upper state will be of $^1\Sigma_u^+$ type and is considered, from the results of vibrational analysis, to be due to $3^2S + 3^2D$ or $3\,^2S + 4\,^2P$ atoms. The values of the molecular constants obtained are:

$B_3'' = 0.152\ cm^{-1}$, $B_4'' = 0.151\ cm^{-1}$, $B_5'' = 0.151\ cm^{-1}$,
$B_2' = 0.103\ cm^{-1}$ and $r'_e = 3.77$ A.

It has not been possible to evaluate a and D from the present data.

INTRODUCTION

Sodium has two systems of bands in the visible, one of which lies in the red and the other in the green region. The rotational structure of the red bands has been studied by Fredrickson (1929) and of the green bands by Smith (1924), Fredrickson and Watson (1927) and by Loomis and Wood (1928). The red bands consist of a single P and a single R branch due to a $^1\Sigma - ^1\Sigma$ transition and the green bands consist of one P one Q and one R branch due to a $^1\Pi - ^1\Sigma$ transition.

Besides the bands in the visible region, Na_2 has a large number of bands in the ultra-violet region which are believed to belong to several systems. Although many attempts have been made at a vibrational analysis of these bands (Pearse and Sinha, 1947; Sinha, 1947, 1948) so far nothing seems to have been done to study their rotational structure. An attempt has, therefore, been made at a rotational analysis of a few bands belonging to the first ultra-violet system of Na_2 which lies between λ3600 and λ3200 A. From this it has been possible to conclude that the bands consist of only two branches and consequently that the upper state is of $^1\Sigma_u^+$ type, the ground state being already known to be $^1\Sigma_g^+$. A rough estimate of the values of B's has also been made. Measurements of the lines and their analysis are given in the following sections:

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EXPERIMENTAL

The experimental arrangement was the same as described before (Sinha, 1948*a*). The bands were photographed in absorption in the first order of a 21-ft. concave grating (dispersion 1.3 Å, per mm.) using a specially built hydrogen discharge tube (Hunter and Pearse, 1936) as source for continuous radiation.

The bands were found to overlap each other and the main concern was to photograph even a few of them without overlapping. For this purpose, a large number of spectra were taken under gradually varying conditions of temperature, pressure and time of exposure. In the spectrograms obtained at lower temperatures (about 550°C), the overlapping could be avoided to a certain extent, but only few lines corresponding to high J values appeared and it was not even possible to ascertain the band to which they belonged. At higher temperatures (about 800°C), there was so much overlapping that it was impossible to use them for any purpose. At intermediate temperatures (650 to 700°C), the overlapping could be overcome to a certain extent in some regions and the structure could also be traced for these bands from near the heads to fairly high J values.

Three bands, λ3432 Å (2, 3), λ3450 Å (2, 4) and λ3468 Å (2, 5) were found most suitable for studying the rotational structure. They are fairly strong bands of the λ3600 – λ3200Å system and had least overlapping when photographed at about 700°C, maintaining nitrogen at a pressure of about 5 cm. of mercury in the absorption chamber. The time of exposure with an Ilford Special Rapid plate was two to three hours.

The bands were degraded to the red. Using values of B′ calculated on the assumption that B_e/ω_e remains constant, it is found that the head is formed by as low as the third or fourth member of the R branch. The low J value lines near the head or the origin are all blended and can be seen resolved only after an interval of 2 to 3Å on the long wavelength side from the head of the band Although the spacing between the lines and their intensity changed in a regular manner on passing to higher and higher members, it was not possible to separate the branches by a mere inspection of the spectrum. Supposing the bands to have only two branches, then for molecules like Na_2 having large moment of inertia, there will not be much difference between the intensity of a P line and the corresponding R line; and since the R branch turns off at something like the third member, the J values of the adjacent lines of each branch will not differ by a large number and consequently the neighbouring P and R branch lines will appear equally intense. If the band has also a third branch, *i.e.*, a Q branch, it will appear with somewhat double the intensity of P or R branch. General appearance did not suggest that a Q branch could be present. It may be further noted that the alternation in intensity due to nuclear spin (nuclear spin of Na = $\frac{3}{2}$) is not well marked on the spectrogram. In fact, a reference

to the spectra published by Loomis and Wood (1928) and by Fredrickson (1929) also indicates the same thing with regard to the above alternation in intensity of the lines.

ROTATIONAL ANALYSIS

It has not been possible to give a very satisfactory analysis of the rotational structure of the bands investigated in the present work. However, it seems fairly conclusive that the lines associated with each of the three bands investigated here can be classified into only two branches, one P and one R arising from the transitions

$$P(J) = F'(J-1) - F''(J)$$

$$\text{and } R(J) = F'(J+1) - F''(J).$$

This suggests that the bands are due to $^1\Sigma - {}^1\Sigma$ transition, and since the ground state is $^1\Sigma_g^+$, the excited state should be of $^1\Sigma_u^+$ type.

An analysis of the rotational structure of these bands is given in Tables I–III. Nearly all the lines measured in this region have been accounted for in these tables. The letter *h* or *d* against a line indicates that it was hazy or an unresolved doublet. It was not possible to make any accurate estimate of the intensity of the lines. In general, however, the higher members were somewhat stronger than the lower ones ; the maximum of the intensity corresponded to members higher than those recorded here, as it was not possible to trace the lines right up to them due to overlapping.

Values of Δ_2F given in columns 4–7 of these tables do not appear very satisfactory. Better results could have been obtained by getting rid of the overlapping, if possible, and obtaining a photoghaph at about three times the dispersion used in the present work. The continuum, however, did not seem to have enough intensity to permit of the latter. The details of the analysis are given below, and since this is the only attempt made to study the rotational structure of the Na_2 ultra-violet bands (rotational structure of the corresponding band systems of even other alkali-metal molecules has not been studied), the results might be of some interest.

As stated before, it is not possible to see the band origion or the low member lines of the branches and, hence, it is not easy to assign correct J values to the lines. Advantage, however, has been taken of the consideration that the lower state for these bands is the same as for the green or red bands for which the rotational constants are known with reasonable accuracy. Therefore, having tentatively arranged the lines into branches, $\Delta_2F''(J)$ which is given by

$$\Delta_2F''(J) = F''(J+1) - F''(J-1) = R(J-1) - P(J+1)$$

can be computed and compared with those calculated with the help of known constants for the ground state, from the formula

$$\Delta_2F''(J) = (4J+2)[B''_v + 2D_v''(J^2+J+1)\ldots].$$

It may be added that these differences for $V''=3$, 4 and 5 with which we are concerned have not been observed in any previous work even for the visible bands and hence the only way to obtain them was with the help of the above formula. From this comparison the arrangement can be checked and correct J values assigned. Although the agreement between the values of $\Delta_2F''(J)$ obtained in the above two ways (last three columns of Tables I-III) is not very satisfactory, yet any attempt to change the J values of the lines even by unity makes the agreement definitely worse and introduces an error which is much greater than can be allowed for experimental errors.

A rough estimate of the molecular constants can be made as follows :

For the ground state constants :

$$\Delta_2F''(J)=R(J-1)-P(J+1)=(4J+2)[B''+2D''(J^2+J+1)].$$

If we neglect D'' (D'' is about 10^6 times smaller than B''), $\Delta_2F''(J)$ varies linearly with J, and if J is correctly known B'' can be evaluated. Further, $\Delta_2F''(J)$ against J will give a straight line, which on extrapolation will intersect $\Delta_2F''(J)=0$ for $J=-\frac{1}{2}$, if J values have been correctly assigned (Fig 1). The value of $\Delta_2F''(J)$ at $J=0$ gives $2B''$.

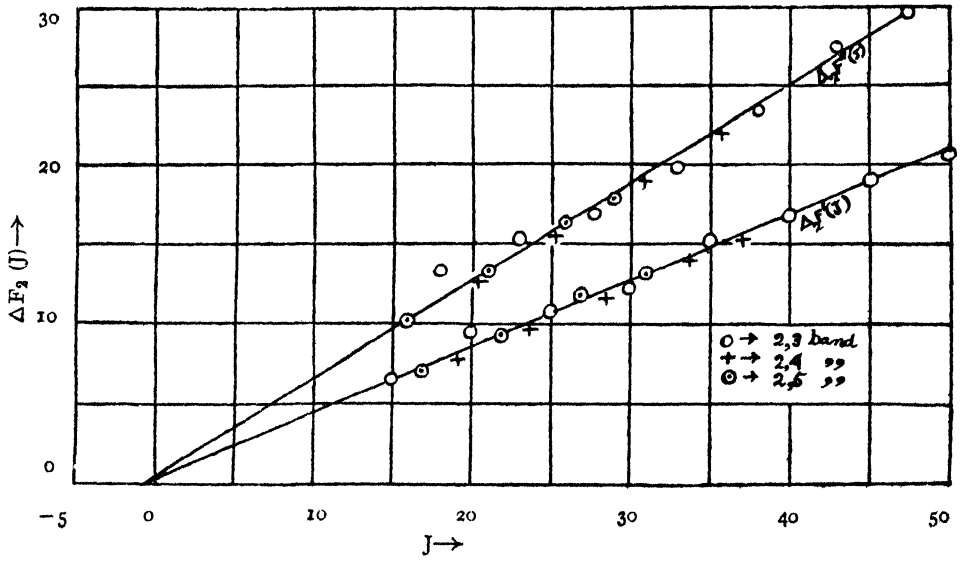

FIG. 1

For the excited state constants :

$$\Delta_2F'(J)=F'(J+1)-F'(J-1)=R(J)-P(J)=(4J+2)[B'+2D'(J^2+J+1)].$$

Neglecting D', B' can be calculated from the above equation. Further, as above, $\Delta_2F'(J)$ varies linearly with J, and extrapolates to 0 at $J=-\frac{1}{2}$ (lower straight line in Fig. 1). The value of $\Delta_2F'(J)$ at $J=0$ gives $2B'$. The values of the constants are given in Table IV.

It may be pointed out that, since the value of B in a given electronic state depends upon the vibrational quantum number, the upper curve in Fig. 1

should really split into three straight lines corresponding to $V''=3$, 4 and 5. The measurements are not however, good enough to resolve the differences between the values of B'' for the three bands, and hence a single straight line passing through the mean positions has been drawn.

It also follows from the equation

$$\nu=\nu_0+(B'+B'')M+(B'-B''+D'-D'')M^2+2(D'+D'')M^3\ldots,$$

where $\nu_0=\nu_e+\nu_v$ and is constant for a band,

$$M=J''+1=1,\ 2,\ldots\text{for R(0), R(1)},\ldots,$$

and $$M=-J'' \quad =-1,\ -2,\ldots\text{for P(1), P(2)},\ldots.$$

TABLE I

Branches and rotational term differences for the λ 3432 Å band of Na_2

J	R(J)	P(J)	$\Delta_2F'(J)$	$\Delta_2F''(J)$	Δ_2F''(calc)	Δ_2F_2(O–C)
14	—	29110.80	—	—	—	—
15	—	09.19	—	—	—	—
16	—	07.16	—	—	—	—
17	29113.43h	05.21	8.22	—	—	—
18	11.73h	03.43	8.30	12.29	11.25	1.04
19	10.04	01.14	8.90	13.21	11.85	1.36
20	08.07	29098.52	9.65	14.15	12.45	1.70
21	05.97	95 89	10.08	14.14	13.05	1.09
22	04.04	94 03	10 01	14.91	13.66	1.25
23	01.89	91.06	10.83	15.43	14.26	1.17
24	29099.45	88.61	10 84	15.49	14.86	0.63
25	96.91	86.40	10.51	15.49	15 46	0 03
26	94.79	83.96	10 83	15.66	16.07	−0.41
27	92.42	81.25	11.17	16 08	16.68	−0.60
28	89 96	78.71	11.25	17.01	17.29	−0.28
29	87.60	75.41	12.19	17 34	17.89	−0.55
30	84 97	72.62	12 35	17.51	18.51	−1.00
31	82.52	70.09	12.43	17.67	19.11	−1.44
32	80.14	67.30	12.84	18.69	19.72	−1.03
33	77.44	63.83	13.61	19.35	20 33	−0.98
34	74.57	60.79	13.87	20.12	20.94	−0.82
35	71.69	57.32	14.67	20 36	21.54	−1.18
36	68.48	54 21	14.27	21.12	22.15	−1.03
37	65.19	50.57h	14.62	22 29	22.76	−0.47
38	62.14	46.19h	15.95	22.13	23.37	−1.24
39	58.93	43.06h	15.87	23.21	23.97	−0 76
40	55.39	38.93h	16 46	24.38	24.57	−0.19
41	51 93h	34.55	17.38	25.57	25.17	0.40
42	48.20h	29.82	18.38	26.57	25.77	0.80
43	44.33h	25.36	19.97	27.73	26.38	1.35
44	40 11h	20.47	19.64	—	26.98	—
45	35.98	—	—	27.98	27.58	0.40
46	31.59	12 13	19.46	28.59	28 19	0.40
47	27.46	07.39	20.07	29.22	28.79	0.43
48	23.08	02.37	20.71	29.46	29.40	0 06
49	18.61	28998 00	20.61	29.96	30.00	−0.04
50	13.81	93.12	20.69	30.54	30.61	−0.07
51	09.10	88.07	21.03	—	—	—
52	04.43	—	—	—	—	—
53	99.50	—	—	—	—	—
54	94.65	—	—	—	—	—
55	89.42	—	—	—	—	—

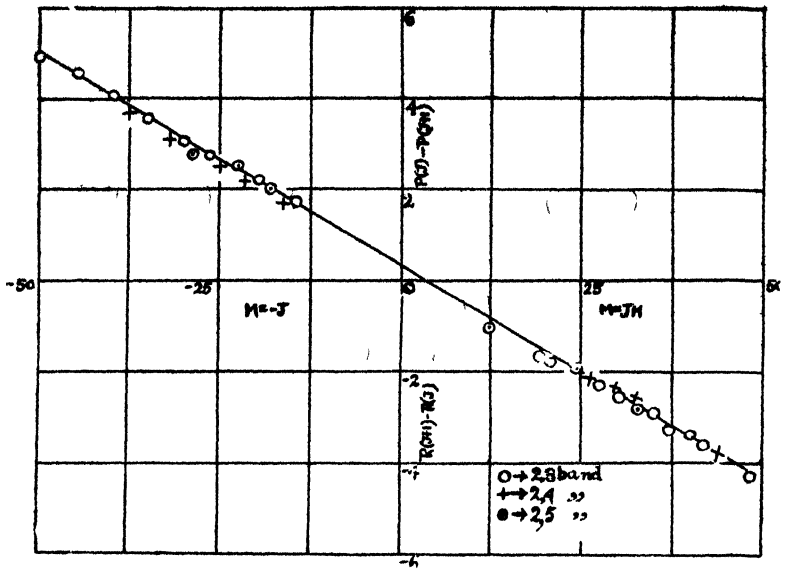

FIG. 2

TABLE II

Branches and rotational term differences for the λ 3450 Å band of Na_2

J	R(J)	P(J)	$\Delta_2F''(J)$	$\Delta_2F'(J)$	Δ_2F''(calc)	Δ_2F''(O−C)
15	28968.00h	28959.61	8.39	—	—	—
16	66.74	58.18	8 56	11.16	9.97	1.19
17	65.31	56.84	8.47	11.83	10 57	1.26
18	63.58	54 91	8.67	12.33	11.17	1.16
19	61.74	52.98	8 76	12.36	11.77	0.59
20	59.61	51 22	8.39	12.69	12.38	0.31
21	57.51	49.05	8.46	—	12.98	—
22	56.00	—	—	12 99	13.58	−0.59
23	54.04	44.52	9.52	13.48	14.18	−0.70
24	52.06	42.42	9 64	13.72	14.78	−1.06
25	49.96	40 32	9.64	13.81	15.38	−1.57
26	47.95	38.35	9.70	14.32	15.98	−1.66
27	45.60	35 64	9.96	14.91	16.57	−1.66
28	43.68	33.04	10.54	15.24	17.16	−1.92
29	41.75	30.36	11.39	16.08	17.76	−1 68
30	39.74	27.60	11.86	17.25	18.35	−1.10
31	37.15	24.50	12.65	18.59	18.94	−0.35
32	34.54	21.15	13.39	19.68	19.53	0.15
33	31.95	17.47	14.48	20.16	20.12	0.04
34	29.03	14.38	14.65	20.75	20.71	0.04
35	25.92	11.20	14.72	20.90	21.30	−0.40
36	22.68	08.13	14 55	21.23	21.89	−0.66
37	19.31	04 69	14 62	22.26	22.48	−0.22
38	15.45	00.42	15.03	23.00	23.07	−0.07
39	11.62	28896.31	15.31	23.21	23.65	−0.44
40	08.13	92.24h	15.89	—	—	—
41	04.69	—	—	—	—	—
42	01.34	—	—	—	—	—
43	28897.83	—	—	—	—	—
44	93.48h	—	—	—	—	—
45	88.97h	—	—	—	—	—

Further if we neglect the D' s, the first differences will vary linearly with M. In other words, R(J−1)−R(J) against J+1, and P(J)−P(J+1) against −J will give a single straight line, intersecting M=0 and M=1 at $2B''$ and $2B'$ respectively (Fig. 2). As pointed out before, in place of three straight lines corresponding to the three values of V″, only one is drawn passing through the mean positions of all the points. The values of B's calculated from Fig. 2 are also given in Table IV.

TABLE III

Branches and rotational term differences for the λ 3468 Å band of Na_2

J	R(J)	P(J)	$\Delta_2F''(J)$	$\Delta_2F''(J)$	Δ_2F''(calc)	Δ_2F''(O−C)
13	28813.54d	28808.15	5.49	—	—	—
14	12.39d	06.49	5.90	9.06	8.74	0.32
15	11.05d	04.49	6.56	9.61	9.34	0.30
16	09.64d	02.75	6 89	9.88	9.94	−0.06
17	08.15d	01.17	6.98	10.40	10.54	−0.14
18	06.49d	28799.26	7.23	10 95	11.13	−0.18
19	04.49d	97.20	7.29	11.45	11.73	−0.28
20	02.75d	95.04	7.61	11.95	12.34	−0.39
21	01.17d	92.54	8.63	12.95	12.94	0.01
22	28799.26d	89 80	9.46	13.89	13.54	0.35
23	97.20d	87.06	10.14	14.68	14.14	0.54
24	95.04d	84.58	10 46	15 50	14-74	0 76
25	93.05	81-70	11.35	15 58	15.33	0.25
26	90.73	79 46	11 27	16.28	15.93	0.35
27	88.25	76.72	11.53	16.82	16.52	0.30
28	85.91	73 91	12.00	17.49	17.10	0.39
29	83.35	70.76	12.69	18 19	17.70	0.49
30	80.87	67.80	12.93	18.06	18 29	−0.23
31	78.46	65.29	13.17	18.80	18 88	−0 08
32	75.90	62.07	13 83	—	—	—
33	73.08	—	—	—	—	—
34	69.19	—	—	—	—	—
35	66.12	—	—	—	—	—
36	62.98	—	—	—	—	—

TABLE IV

Values of B″ and B′ for the states of λ3600 – λ3200 Å system of Na_2 bands

Method used	$B''(cm^{-1})$			$B'(cm^{-1})$		
	2, 3 band	2, 4 band	2, 5 band	2, 3 band	2, 4 band	2, 5 band
From Δ_2F	0.152	0.151	0.151	0.105	0.102	0.103
From Fig.1		0 15			0.10	
From Fig.2		0.15			0.10	
Loomis & Wood	0.1518	0.1515	0.1510			

Mean value of B′ is 0.103 cm^{-1} approx. and from this $r_e' = 3.77$ Å. approx.

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